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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]In this invention, it is related with the container formed from the cyclic olefin system copolymer.

Therefore, it is related with the cyclic olefin system copolymer container with which contamination by fingerprint adhesion of an outside surface etc. was canceled more by details.

[0002]

[Description of the Prior Art]Its attention is paid to the cyclic olefin system copolymer in the field of transparent packaging material as olefin system resin which was excellent in transparency or waterproof part permeability, and was excellent also in heat resistance or a mechanical property.

[0003]From the cyclic olefin system copolymer, manufacturing blow molded containers, such as a bottle, is also already known, and the blow molded article fabricated from the copolymer which carries out addition condensation of cyclic olefin and the ethylene is indicated to JP,H3-726,A. The stretch-blow-molding article which changes from the polyolefine which has 5 thru/or 60 mol of cyclic olefin ingredient % to JP,H7-80919,A is indicated.

[0004]

[Problem to be solved by the invention]Although divided roughly into the container which comprises a cyclic olefin system copolymer by the blow molding container which is not extended by the injection blowing method etc., and the stretch-blow-molding container by a cold parison process etc., The intensity to a dropping impact is low and the container which performed extension shaping is excellent in the unextended blow molding container in respect of the practicality of a container.

[0005]However, it turned out that the unextended container made from a cyclic olefin system

copolymer has one fault which is not accepted at all at the cyclic olefin system copolymer container which performed extension shaping. That is, if the extension molded container made from a cyclic olefin system copolymer is touched, the fingerprint of a fingertip will shift to a container surface and will produce white muddiness on the surface. Since this phenomenon is not accepted at all with the container of an unextended cyclic olefin system copolymer, the problem of the surface contamination in an extension molded container is presumed to be what is closely connected with the molecular orientation of a cyclic olefin system copolymer. [0006] This invention persons found out that generating of the dirt by fingerprint adhesion of the outside surface in the extension molded container of a cyclic olefin system copolymer was thoroughly prevented by making the molecular orientation of this extension molded container outside surface ease.

[0007] That is, the purpose of this invention has generating of the dirt by fingerprint adhesion of an outside surface in providing the extension molded container made from a cyclic olefin system copolymer prevented thoroughly.

[0008]

[Means for solving problem] In the container with which the outside surface of the container was formed from the cyclic olefin system copolymer at least according to this invention, Molecular orientation of the cyclic olefin system copolymer of a container which forms a drum section at least is carried out to at least 1 shaft orientations, And the molecular orientation of the cyclic olefin system copolymer of a container outside surface is eased, A container, wherein a haze value when the spreading examination of the outside surface of a container is done with the mixture of an aliphatic series petroleum distillate (CAS No.8052-41-3) and a petroleum base oil (CAS No.64742-65-0) is less than 20% is provided.

[0009] Although the molecular orientation of the cyclic olefin system copolymer of a container outside surface is eased in the container of this invention, When relaxation of this molecular orientation forms a container from (A) preforming, Even if carried out by considering it as the temperature distribution that molecular orientation is held inside and molecular orientation is eased in an outside surface, Or it may be carried out from heat treatment of (B) container outside surface, especially heat treatment that the outside-surface temperature of the container at the time of heat treatment will be not less than 130 **, and may be performed by the flame treatment of (C) container outside surface.

[0010] In this invention, a cyclic olefin system copolymer depends on excelling in transparency or surface glossiness and moreover excelling forming an outside surface from a cyclic olefin system copolymer at least of a container also in waterproof steamy permeability. Making at least 1 shaft orientations carry out molecular orientation of the cyclic olefin system copolymer of a container which forms a drum section at least to 2 shaft orientations suitably, In the undivided-oriented state, the cyclic olefin system copolymer is remarkably inferior to shock

resistance, and it is for shock resistance to improve remarkably by giving this molecular orientation.

[0011]The outside surface of this extension molded container so that a haze value when a spreading examination is done with the mixture (it may only be called a petroleum mixture below) of an aliphatic series petroleum distillate (CAS No8052-41-3) and a petroleum base oil (CAS No64742-65-0) may be less than 20%, It is the remarkable feature to have carried out orientation relaxation, and, thereby, generating of the dirt by fingerprint adhesion of an outside surface can be prevented thoroughly.

[0012]Generally, although the grade of the molecular orientation of a polymer is estimated by a double reflex, an X diffraction, densimetry, deviation fluorescence method, etc., In that a cyclic olefin system copolymer is intrinsically amorphous, thru/or it is a low crystal and the container which is the objects of this invention, It was difficult to evaluate the grade of relaxation of molecular orientation, or the grade of remains of molecular orientation by the conventional technique from orientation relaxation of a cyclic olefin system copolymer having arisen only within the thin layer of an outside surface.

[0013]The close relation between the grade of the molecular orientation of a cyclic olefin system copolymer and a haze value when the spreading examination of the above-mentioned petroleum mixture is done at a cyclic olefin system copolymer was, and moreover, according to this measuring method, this invention persons found out that the grade of the molecular orientation of a thin layer could also be evaluated correctly. That is, with an undivided-oriented cyclic olefin system copolymer molded product, also when a spreading examination is done with a petroleum mixture, if a spreading examination is done with a petroleum mixture, in the cyclic olefin system copolymer by which extension shaping was carried out to not producing a white blush mark at all, a white blush mark will be produced clearly.

[0014]The angle in the X diffraction image measured using minute X-ray diffractometer the grade of the molecular orientation in the extension molded container of a cyclic olefin system copolymer (2 theta) It turned out that it can evaluate also by half peak width computed from the peak area of the range from 7.241 degrees to 23.241 degrees. Drawing 1 is an X diffraction image of the stretch-blow-molding bottle of a cyclic olefin system copolymer, drawing 2 is an X diffraction image of the melting blow molding bottle of a cyclic olefin system copolymer, and drawing 3 is an X diffraction image of what performed the frame process to the surface of the stretch-blow-molding bottle of a cyclic olefin system copolymer. The relation between a processing condition and half peak width is shown about the bottle into which Table 1 mentioned later changed the conditions of the three above-mentioned kinds of bottles, and a frame process. With these results to a melting blow molding bottle, half peak width is the smallest, and it turns out that half peak width becomes narrow with a stretch-blow-molding bottle, so that half peak width is these middle and a processing condition becomes an elevated

temperature with the stretch-blow-molding bottle which half peak width was the largest and carried out the frame process. Although the Reason which such a phenomenon produces is not yet clear enough, it is considered because distortion is in the state small more near homogeneity with an unextended bottle to one random [distortion of an inside], and large with an extension shaping bottle. However, the whole thickness direction of the container is made into the measuring object, and it excels in the measuring means by an X diffraction only to the value as average value of the whole thickness direction being measured with the point which makes only the surface the measuring object in the spreading examination by a petroleum mixture.

[0015]In this invention, generating of the dirt by fingerprint adhesion of an outside surface can be thoroughly prevented by carrying out orientation relaxation of the cyclic olefin system copolymer of the thin layer of an outside surface so that a haze value when a spreading examination is done with a specific petroleum mixture may be less than 20%, as shown in the example mentioned later. And since it was restricted to the surface thin layer that molecular orientation relaxation is carried out and molecular orientation remains in the cyclic olefin system copolymer of most container walls, the advantage of being maintained without shock resistance falling on parenchyma is also acquired.

[0016]

[Mode for carrying out the invention]In drawing 4 (side view) in which an example of the container of this invention is shown, this container 1 is formed by the stretch blow molding of the cyclic olefin system copolymer, the drum section 2, the blockade pars basilaris ossis occipitalis 3, and the neck 4 are comprised, and the screw 5 for cap engagement is formed in the neck 4.

[0017]In drawing 5 in which the section structure of a container drum part is shown, orientation of the container wall 6 is carried out by biaxial stretching, and by the thin layer 7 of the outside surface, orientation relaxation is carried out so that a haze value when a surface treatment is carried out with a petroleum mixture may be less than 20%. Drawing 5 does not show the actual thickness ratio of the thin layer 7 by which orientation relaxation was carried out, and it should be understood that the existence is emphasized.

[0018]As a cyclic olefin system copolymer of a container which constitutes an outside surface at least, amorphous thru/or the low crystal copolymer (COC) of an olefin and cyclic olefin are used.

[0019]As an olefin which constitutes a copolymer, although ethylene is preferred, others -- the alpha olefin of the carbon numbers 3 thru/or 20, such as propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 3-methyl-1-pentene, and 1-decene, is independent, or is used in combination with ethylene.

[0020]As cyclic olefin, fundamentally, although it is an alicycle fellows hydrocarbon compound

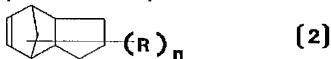
which has an ethylene system unsaturated bond and a bicyclo ring, especially a hydrocarbon compound which has a bicyclo[2, 2, 1]hept 2-ene skeleton and the following are specifically mentioned, of course, it is not limited to this.

[0021]Bicyclo[2.2.1]hept 2-ene derivative; (1), for example, a following formula
[Chemical formula 1]



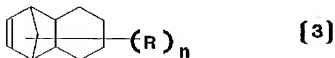
the bicyclo[2.2.1]hept 2-ene derivative whose R is a hydrogen atom, an alkyl group, a cycloalkyl group, or an alkylidene group among a formula, whose n is the number of 1-4 (it is the same as that of the following) and which is come out of and expressed. Especially, The bicyclo-[[2.2.1] hept 2] ene 6-methylbicyclo[2.2.1]hept 2-ene 5, 6-dimethylbicyclo[2.2.1]hept 2-ene 1-methylbicyclo[2.2.1]hept 2-ene 6-ethylbicyclo[2.2.1]hept 2-ene 6-n - Butylbicyclo[2.2.1]hept 2-ene 6-isobutylbicyclo[2.2.1]hept 2-ene 7-methylbicyclo[2.2.1]hept 2-ene.

[0022]Tricyclo [4.3.0.1^{2,5}]-3-decene derivative; (2), for example, a following formula
[Chemical formula 2]



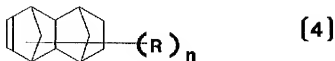
The tricyclo [4.3.0.1^{2,5}]-3-decene derivative come out of and expressed. In particular, it is tricyclo [4.3.0.1^{2,5}]-3-Decene 2-methyl tricyclo [4.3.0.1^{2,5}]-3-decene 5-methyl tricyclo [4.3.0.1^{2,5}]-3-decene.

[0023]Tricyclo [4.4.0.1^{2,5}]-3-undecene derivative; (3), for example, a following formula
[Chemical formula 3]



The tricyclo [4.4.0.1^{2,5}]-3-undecene derivative come out of and expressed. Especially, tricyclo [4.4.0.1^{2,5}]-3-undecene 10-methyl tricyclo [4.4.0.1^{2,5}]-3-undecene.

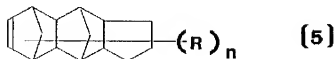
[0024]A tetracyclo [4.4.0.1^{2,5}.1^{7,10}]-3-dodecen derivative (4), for example, a following formula
[Chemical formula 4]



The tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen derivative come out of and expressed. Especially, Tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-Dodecen 8-methyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-ethyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-, [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8- the propyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8. [- butyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-isobutyl tetracyclo] hexyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-cyclohexyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-stearyl tetracyclo -- [4.4.0.1^{2.5}.1^{7.10}]-3-. The dodecen 5, The 10-dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 2, 10 - Dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8,9-dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-E. The ****- 9-methyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 11, The 12-dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 2, 7,9-trimethyl tetracyclo one -- the [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 2,7-dimethyl- 9-ethyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 9-isobutyl- 2. The 7-dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 9, 11,12-trimethyl tetracyclo one -- [4.4.0.1^{2.5}.1^{7.10}] -- the-3-dodecen 9-ethyl-11,12-dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 9-isobutyl- 11. The 12-dimethyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 5, 8,9,10-tetramethyl tetracyclo one -- [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-ethylidene tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-ethylidene-9-MECHIRUTETO. RASHIKURO [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-ethylidene-9-ethyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-ethylidene-9-isopropyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-ethylidene-9-butyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-n-propylidene tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-n-propylidene-9-. Methyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-n - Propylidene-9-ethyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-n-propylidene-9-isopropyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-n - Propylidene-9-butyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-isopropylidene tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8. - The isopropylidene- 9. - Methyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8 - Isopropylidene-9-ethyltetracyclo-3- [[4.4.0.1^{2.5}.1^{7.10}]] dodecen 8-isopropylidene-9-isopropyltetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-isopropylidene-9-butyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen. [0025]Pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4-pentadecene derivative; (5), for example, a following

formula

[Chemical formula 5]



The pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4-pentadecene derivative come out of and expressed.

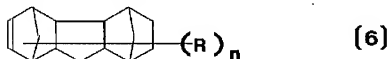
Especially, Pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4-pentadecene-1, 3-dimethyl pentacyclo

[6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4-pentadecene-1, the 6-dimethyl pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4-

pentadecene 14, 15-dimethyl pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4-pentadecene.

[0026]A pentacyclo [7.4.0.1^{2.5}.1^{9.12}.0^{8.13}]-3-pentadecene derivative (6), for example, a following formula

[Chemical formula 6]



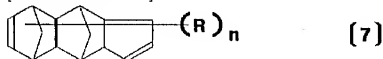
The pentacyclo [7.4.0.1^{2.5}.1^{9.12}.0^{8.13}]-3-pentadecene derivative come out of and expressed.

Especially, pentacyclo [7.4.0.1^{2.5}.1^{9.12}.0^{8.13}]-3-pentadecene methylation pentacyclo

[7.4.0.1^{2.5}.1^{9.12}.0^{8.13}]-3-pentadecene.

[0027]A pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4,10-pentadeca diene derivative (7), for example, a following formula

[Chemical formula 7]

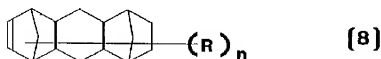


The pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4,10-pentadeca diene derivative come out of and expressed.

In particular, it is pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4,10-pentadecadiene.

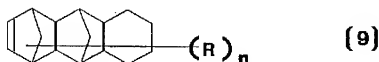
[0028]A pentacyclo [8.4.0.1^{2.5}.1^{9.12}.0^{8.13}]-3-hexa decene derivative (8), for example, a following formula

[Chemical formula 8]



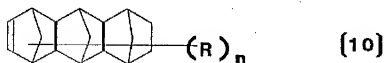
The pentacyclo [8.4.0.1^{2,5}.1^{9,12}.0^{8,13}]-3-hexa decene derivative come out of and expressed. Especially, Pentacyclo [8.4.0.1^{2,5}.1^{9,12}.0^{8,13}]-3-hexa decene 11-methyl-pentacyclo [8.4.0.1^{2,5}.1^{9,12}.0^{8,13}]-3-hexa decene 11-ethyl-pentacyclo [8.4.0.1^{2,5}.1^{9,12}.0^{8,13}]-3-hexa decene 10,11-dimethyl- pentacyclo [8.4.0.1^{2,5}.1^{9,12}.0^{8,13}]-3-hexa decene. [0029]pentacyclo [6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexa decene derivative (9), for example, a following formula,

[Chemical formula 9]



The pentacyclo [6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexa decene derivative come out of and expressed. Especially, The pentacyclo [6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexa decene 1, The 3-dimethyl pentacyclo-4-[[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]] hexa decene 1,6-dimethyl pentacyclo [6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexa decene 15, 16-dimethyl pentacyclo [6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexa decene. [0030]A hexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene derivative (10), for example, a following formula

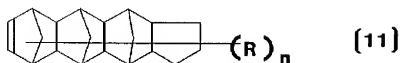
[Chemical formula 10]



The hexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene derivative come out of and expressed. Especially, Hexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene 12-methylhexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene 12-. The ethylhexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene 12-isobutylhexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene 1, 6,10-trimethyl 12-isobutylhexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-4-heptadecene.

[0031]A heptacyclo [8.7.0.1^{2,9}.1^{4,7}.1^{11,17}.0^{3,8}.0^{12,16}]-5-eicosen derivative (11), for example, a following formula

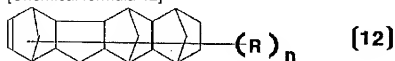
[Chemical formula 11]



The heptacyclo [8.7.0.1^{2.9}.1^{4.7}.1^{11.17}.0^{3.8}.0^{12.16}]-5-eicosen derivative come out of and expressed. In particular, it is heptacyclo [8.7.0.1^{2.9}.1^{4.7}.1^{11.17}.0^{3.8}.0^{12.16}]-5-eicosen.

[0032]A heptacyclo [8.7.0.1^{3.6}.1^{10.17}.1^{12.15}.0^{2.7}.0^{11.16}]-4-eicosen derivative (12), for example, a following formula

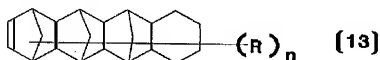
[Chemical formula 12]



The heptacyclo [8.7.0.1^{3.6}.1^{10.17}.1^{12.15}.0^{2.7}.0^{11.16}]-4-eicosen derivative come out of and expressed. Especially, Heptacyclo [8.7.0.1^{3.6}.1^{10.17}.1^{12.15}.0^{2.7}.0^{11.16}]-4-eicosen dimethyl substitution heptacyclo [8.7.0.1^{3.6}.1^{10.17}.1^{12.15}.0^{2.7}.0^{11.16}]-4-eicosen.

[0033]A heptacyclo [8.8.0.1^{2.9}.1^{4.7}.1^{11.18}.0^{3.8}.0^{12.17}]-5-strange eicosen derivative (13), for example, a following formula

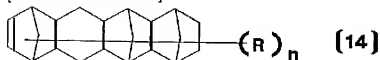
[Chemical formula 13]



The heptacyclo [8.8.0.1^{2.9}.1^{4.7}.1^{11.18}.0^{3.8}.0^{12.17}]-5-strange eicosen derivative come out of and expressed. In particular, it is heptacyclo [8.8.0.1^{2.9}.1^{4.7}.1^{11.18}.0^{3.8}.0^{12.17}]-5-strange eicosen.

[0034]heptacyclo [8.8.0.1^{4.7}.1^{11.18}.1^{13.16}.0^{3.8}.0^{12.17}]-5-strange eicosen derivative (14), for example, a following formula,

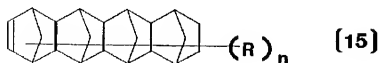
[Chemical formula 14]



The heptacyclo [8.8.0.1^{4.7}.1^{11.18}.1^{13.16}.0^{3.8}.0^{12.17}]-5-strange eicosen derivative come out of and expressed. Especially, Heptacyclo [8.8.0.1^{4.7}.1^{11.18}.1^{13.16}.0^{3.8}.0^{12.17}]-5-strange eicosen 15-methyl-heptacyclo [8.8.0.1^{4.7}.1^{11.18}.1^{13.16}.0^{3.8}.0^{12.17}]-5-strange eicosen trimethyl substitution heptacyclo [8.8.0.1^{4.7}.1^{11.18}.1^{13.16}.0^{3.8}.0^{12.17}]-5-strange eicosen.

[0035]An octacyclo [8.8.0.₁^{2.9}₁^{4.7}₁^{11.18}₁^{13.16}₀^{3.8}₀^{12.17}]-5-docosene derivative (15), for example, a following formula

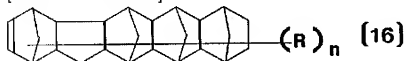
[Chemical formula 15]



The octacyclo [8.8.0.₁^{2.9}₁^{4.7}₁^{11.18}₁^{13.16}₀^{3.8}₀^{12.17}]-5-docosene derivative come out of and expressed. Especially, Octacyclo [8.8.0.₁^{2.9}₁^{4.7}₁^{11.18}₁^{13.16}₀^{3.8}₀^{12.17}]-5-docosene 15-methyl octacyclo [8.8.0.₁^{2.9}₁^{4.7}₁^{11.18}₁^{13.16}₀^{3.8}₀^{12.17}]-5-docosene 15-ethyl octacyclo [8.8.0.₁^{2.9}₁^{4.7}₁^{11.18}₁^{13.16}₀^{3.8}₀^{12.17}]-5-docosene.

[0036]A nonacyclo [10.9.1.₁^{4.7}₁^{13.20}₁^{15.18}₀^{2.10}₀^{3.8}₀^{12.21}₀^{14.19}]-5-pentacosene derivative (16), for example, a following formula

[Chemical formula 16]

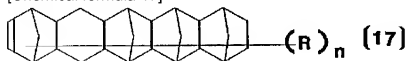


The nonacyclo [10.9.1.₁^{4.7}₁^{13.20}₁^{15.18}₀^{2.10}₀^{3.8}₀^{12.21}₀^{14.19}]-5-pentacosene derivative come out of and expressed. Especially, Nonacyclo

[10.9.1.₁^{4.7}₁^{13.20}₁^{15.18}₀^{2.10}₀^{3.8}₀^{12.21}₀^{14.19}]-5-pentacosene trimethyl substitution nonacyclo [10.9.1.₁^{4.7}₁^{13.20}₁^{15.18}₀^{2.10}₀^{3.8}₀^{12.21}₀^{14.19}]-5-pentacosene.

[0037]A nonacyclo [10.10.1.₁^{5.8}₁^{14.21}₁^{16.19}₀^{2.11}₀^{4.9}₀^{13.22}₀^{15.20}]-6-hexacosene derivative (17), for example, a following formula

[Chemical formula 17]



The nonacyclo [10.10.1.₁^{5.8}₁^{14.21}₁^{16.19}₀^{2.11}₀^{4.9}₀^{13.22}₀^{15.20}]-6-hexacosene derivative come out of and expressed. In particular, it is nonacyclo

[10.10.1.₁^{5.8}₁^{14.21}₁^{16.19}₀^{2.11}₀^{4.9}₀^{13.22}₀^{15.20}]-6-hexacosene.

[0038]The following can also be mentioned as other examples of cyclic olefin.

5-phenyl-bicyclo[2.2.1]hept 2-ene 5-methyl-5-phenyl-bicyclo[2.2.1]hept 2-ene 5-benzyl-bicyclo

[2.2.1]hept 2-ene 5-tolyl bicyclo[2.2.1]hept 2-ene 5-. (Ethylphenyl)-bicyclo[2.2.1]hept 2-ene 5- (isopropylphenyl)- Bicyclo[2.2.1]hept 2-ene 5 -(biphenyl)- Bicyclo[2.2.1]hept 2-ene 5 -(beta-naphthyl)- Bicyclo[2.2.1]hept 2-ene 5-. The (alpha-naphthyl)-bicyclo[2.2.1]hept 2-ene 5-(anthracenyl)-bicyclo[2.2.1]hept 2-ene 5,6-diphenyl-bicyclo[2.2.1]hept 2-ene cyclopentadiene-acenaphthylene adduct 1,4-methano- 1 and 4, The 4a,9a-tetrahydro fluorene 1,4-methano- 1 and 4, 4a,5,10,10a-hexahydroanthracene 8 - Phenyl-tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-methyl-8-phenyl-tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8. - Benzyl-tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-tolyl tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8 -(ethylphenyl)- Tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3. - Dodecen 8-. The (isopropylphenyl)-tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8, 9-diphenyl-tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-(biphenyl) tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-(beta-naphthyl) tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8-. (alpha naphthyl)-tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen 8 -(anthracenyl)- to tetracyclo [4.4.0.1^{2.5}.1^{7.10}]-3-dodecen (cyclopentadiene-acenaphthylene adduct). Compound 11,12-benzo-pentacyclo [6.5.1.1^{3.6}.0^{2.7}.0^{9.13}]-4 which added the cyclopentadiene further. - The pentadecene 11, The 12-benzo-pentacyclo-4-[[6.6.1.1^{3.6}.0^{2.7}.0^{9.14}]] hexa decene 11-phenyl-hexacyclo [6.6.1.1^{3.6}.10.13.0^{2.7}.0^{9.14}]-4-heptadecene 14, 15-benzo-heptacyclo [8.7.0.1^{2.9}.1^{4.7}.1^{11.1}.7.0^{3.8}.0^{12.16}]-5-eicosen]

[0039]Especially this copolymer (COC) is good to be derived from 40 thru/or 22-mol% of cyclic olefin, and residual ethylene, and to have 200 ** or less of 150 thru/or 60 ** glass transition points (Tg) especially, 50 thru/or 22-mol%.

[0040]It is good to measure the molecular weight of this copolymer at 135 ** among a decalin, although there is no restriction in particular, and to have the limiting viscosity [eta] of 0.1 thru/or 20 dl/g, and that degree of crystallinity is measured with an X-ray diffraction method, and, generally is especially 5% or less 10% or less.

[0041]The above-mentioned copolymer (COC) is obtained by carrying out random polymerization of an olefin and the cyclic olefin in itself under existence of a publicly known vanadium system catalyst or a metallocene system catalyst. A suitable copolymer (COC) may be obtained with the trade name of APEL from Mitsui petrochemical incorporated company.

[0042]Although using independently is preferred as for a cyclic olefin system copolymer, they are the range which does not spoil the essence, i.e., a quantity smaller than 50 weight %, and 30 or less weight % of quantity, and can also be used in the form of mixed material with other olefin system resin. As other olefin system resin, an olefin system homopolymer and a copolymer are used suitably. For example, lower density, semi-gross density or high-density polyethylene, linear low density polyethylene, Polypropylene, the polybutene 1, the polypentene- 1, the poly 4-methylpentene- 1, a propylene-ethylenic copolymer, an ionomer, an

ethylene-acrylic copolymer, an ethylene-vinylacetate copolymer, etc. can be mentioned. Of course, even if these olefin system resin is independent, it can use even two or more sorts of combination.

[0043]Generally especially these olefin system resin to blend is good 0.1 thru/or 50g / to have MFR (melt flow rate) of 0.2 thru/or 30g / 10min 10 min, and can carry out selection use of the thing of an extrusion grade, or the thing of an injection grade suitably according to a molding method.

[0044]A publicly known combination drug, for example, paints, a bulking agent, an antioxidant, lubricant, stabilizer, an ultraviolet ray absorbent, etc. can be blended with the above-mentioned cyclic olefin system copolymer according to a publicly known formula in itself.

[0045]An extrusion machine and a catapult are supplied, after carrying out melt kneading of a cyclic olefin system copolymer or its constituent, thermoforming of it is carried out to a preforming object, and subsequently a preforming object is fabricated in an arbitrary-shaped container by carrying out extension shaping. Under the present circumstances, it is preferred to carry out melt kneading at temperature with a glass transition temperature of +200 ** or less, especially temperature with a glass transition temperature of +150 ** or less.

[0046]The extrusion machine provided with arbitrary screws as an extrusion machine is used suitably. A flat die and a ring die can be used as a dice.

[0047]As a catapult, what is publicly known in itself provided with the injection plunger or the screw is used, and said mixture is ejected in an ejected type through a nozzle, a sprue, and a gate. Thereby, resin flows in an injection mold cavity, cooling solidification is carried out and preforming articles, such as preforming, are obtained.

[0048]When manufacturing a container, like a cold parison process, a preforming object can once be manufactured and extension shaping of this preforming object can be carried out at the last mold goods. For example, by injection moulding, fabricate smaller [than a container]-shaped closed-end preforming, and a gas is blown into this closed-end preforming, and it pulls and extends to shaft orientations and is considered as a biaxial-stretching shaping bottle. a sheet -- after thermoforming and plug assist forming -- pressure forming is carried out and it is considered as an extension cup like container. Under the present circumstances, molecular orientation of the container wall is carried out to a height direction (1 shaft orientations).

[0049]Although extension shaping is based also on the kind (glass transition point) of resin, generally it chooses 70 thru/or 200 ** of suitable extension molding temperature from the range of 80 thru/or 180 ** according to the kind of resin especially. Draw magnification is area magnification and 1.3 thru/or 16 times as many ranges are especially 1.2 thru/or 20 times more suitable for it.

[0050]The form etc. of the container used for this invention of a bottle, a cup, a tube, and a plastic can may be arbitrary, for example. Even if this container is a container of the monolayer

of a cyclic olefin system copolymer, As long as the outside surface is formed with the cyclic olefin system copolymer, as other thermoplastics which may be a laminated container with other thermoplastics and is laminated, For example, low density polyethylene, high density polyethylene, polypropylene, A poly 1-butene, poly-4-methyl-1-pentene, or ethylene, Polyolefines, such as random or a block copolymer of alpha olefin comrades, such as PIROPIREN, 1-butene, and 4-methyl-1-pentene, An ethylene-vinyl acetate copolymer, an ethylene vinyl alcohol copolymer, Ethylene vinyl compound copolymers, such as an ethylene vinyl chloride copolymer, Styrene resin, such as polystyrene, an acrylonitrile styrene copolymer, ABS, and a alpha-methylstyrene styrene copolymer, Polyvinyl chloride, a polyvinylidene chloride, a vinyl chloride vinylidene chloride copolymer, Polyamide, such as polyvinyl compound [, such as poly(methyl acrylate) and poly methyl methacrylate,], nylon 6, and nylon 6-6 and nylon 6-10, Nylon 11, and Nylon 12, polyethylene terephthalate, Those mixtures [, such as thermoplastic polyester polycarbonate, and polyphenylene oxide,], such as polybutylene terephthalate, can be mentioned.

[0051]In this invention, the cyclic olefin system copolymer of the thin layer of the outside surface of a container drum part, Orientation relaxation is carried out so that a haze value when a spreading examination is done with the mixture of an aliphatic series petroleum distillate (CAS No.8052-41-3) and a petroleum base oil (CASNo.64742-65-0) may be less than 20%.

[0052]The petroleum mixture used for measurement of the grade of orientation or orientation relaxation may be obtained with the trade name of WD-40 (registered trademark) from WD-40 company of San Diego, California, U.S. According to the data sheet of the company, this product is an aliphatic series petroleum distillate as an ingredient. CAS No.8052-41-3 0 > 20% of 70% petroleum base-oil CAS No.64742-65-innocence ingredient It is a thing containing <10%, as physical properties -- the boiling point : The 300-degree-F (149 **) minimum vapor density (air =1): -- one -- a large -- Water solubility : Insoluble Specific gravity (water =1) : -- 0.800 (70 degrees F (21 **))

Volatile matter content (volume) : it has 74%.

[0053]According to CAS (Chemical-Abstracts service), the above-mentioned 8052-41-3 is called under the name of a naphtha solvent, is colorless refining petroleum distillates without the smell attached to a nose, or a nasty smell, and is defined as what is boiled in about 149 ** thru/or 204.5 **. The above-mentioned 64742-65-0 is called under the name of a solvent DEWAKKUSUDO heavy paraffinic distillate, The hydrocarbon which mainly has a carbon number of the range of C20 thru/or C50 is made into a subject, and it defines as the compound combination of the hydrocarbon obtained by removing a normal paraffin by solvent crystallization of a petroleum fraction as oil which has the viscosity of 19 or more centistokes at 40 **.

[0054]Spreading examination to the cyclic olefin system copolymer by the above-mentioned petroleum mixture and measurement of a haze value are performed by the method given in an embodiment mentioned later.

[0055]In this invention, if orientation relaxation of a cyclic olefin system copolymer is performed about the thin layer of an outside surface, it is enough, and specifically, it is good to carry [5 thru/or 500-micrometer] out over the range of 10 thru/or 300 micrometers suitably. That is, when there is a tendency it to become difficult to perform uniform molecular orientation relaxation over the whole surface if less than a mentioned range and it exceeds a mentioned range on the other hand, the grade of the loss of molecular orientation becomes large and there is a tendency for shock resistance to fall.

[0056]In this invention, a means in particular to perform orientation relaxation so that the above-mentioned requirements may be satisfied is not limited, but can be performed in the manufacturing stage of an extension molded container, or the arbitrary stages after manufacture of an extension molded container.

[0057]For example, an advantageous and easy method is a method of giving the temperature distribution that molecular orientation is held inside and molecular orientation is eased in an outside surface, and performing extension shaping, on manufacture. That is, it is a method maintains only the surface portion which should serve as a container outside surface of preforming which should be carried out stretch blow molding, or the sheet which should be carried out extension sheet forming to an elevated temperature rather than extension temperature (temperature which molecular orientation produces), performs extension shaping, and keep orientation from producing in the thin layer of an outside surface. being based general on extension molding temperature (T_0) although cooking temperature for this is different also by the glass transition point of a cyclic olefin system copolymer -- T_0 -- not less than 10 ° of temperature requirements beyond T_0+15 ° are especially suitable. After heating preforming or a sheet to extension molding temperature, alternative heating of only a surface portion irradiates a drum section outside surface with infrared rays, heats an outside surface to the above-mentioned temperature, or heats the whole preforming to the above-mentioned temperature requirement, and it should just perform extension shaping, cooling an inside on the occasion of extension shaping.

[0058]The inner surface temperature of the metallic mold used for stretch blow molding or extension sheet forming is maintained to the above-mentioned orientation relaxation temperature as an exception method, the outside surface of the container currently fabricated contacts a metallic mold, and orientation may be made to be eased. In this case, cooling of a container can be performed by blowing the fluid for cooling into the inside of a container. The thickness of an orientation mitigation layer is controllable by adjusting the contact time of the temperature metallurgy type of a metallic mold, and a container outside surface.

[0059]Orientation relaxation of extension shaping and a container outside surface can also be performed by an one-step method as mentioned above, and it can also carry out with a two step method. After in the case of a two step method performing only extension shaping within the first step of metallic mold, and performing orientation relaxation within the second step of metallic mold and performing extension shaping within the first step of metallic mold, orientation relaxation by heating of an outside surface may be performed out of a metallic mold, and the last blow molding may be performed within the second step of metallic mold.

[0060]Orientation relaxing treatment by flame treatment etc. can also be performed to the container after extension shaping.

[0061]Although arbitrary heat sources, such as heating by a flame, infrared heat, and dielectric heating, are used as a heat source of orientation relaxing treatment, since it can heat efficiently to the inside of the simplicity of operation, and a short time, flame treatment is the most suitable.

[0062]In that performing flame treatment in the state of a perfect reducing flame does not cause combustion or oxidation of a melting parison, it is important and arbitrary fuel gas, such as town gas, propane, liquefied natural gas, and liquefied petroleum gas, is used as fuel. The result it should be satisfied with this invention of a result if it heats so that burner temperature may generally be made into the temperature of 1200 thru/or 1400 **, the interval of a burner tip and a container surface may be 20 thru/or about 40 mm and the whole drum section surface may contact a burner tip is obtained.

[0063]Plasma treatment etc. may be performed in the cyclic olefin system copolymer nature container after extension shaping, and orientation relaxation of the thin layer of an outside surface may be performed in it.

[0064]If it is equipment which produces plasma discharge, such as high frequency discharge, microwave discharge, or glow discharge, as equipment used for plasma treatment, it may be arbitrary and will be used as a treatment atmosphere in being [pass and / RIUMU etc. / independent] or two-sort [air, nitrogen, oxygen, argon, and] or more combination. As for especially ambient pressure power, it is preferred that there is generally 0.1 thru/or 10 Torr in the range of 0.5 thru/or 5Torr. processing energy -- 20 thru/or 300W -- especially the range of 50 thru/or 200W is suitable -- processing time -- 1 -- or 5 thru/or especially 300 seconds are preferred for 600 seconds.

[0065]

[Working example]Although the following examples explain this invention concretely, this invention is not limited to the following examples. In the following examples, the examination was done as follows.

[0066]** Petroleum mixture WD-40 (registered trademark) was uniformly applied to the surface of the measurement test portion of a molecular orientation degree (haze value) so that the

coverage per surface area might become 0.2 mg/cm^2 , and it was settled on it for 10 minutes at 23 °C and RH50% of atmosphere. About the sample after spreading, the haze value was measured using SM color computer (made by Suga Test Instruments Co., Ltd.).

[0067]** After touching the test portion container of the surface dirt by fingerprint adhesion by a hand for several minutes, the existence of fingerprint adhesion was observed. The haze value was measured using SM color computer (made by Suga Test Instruments Co., Ltd.). The following standard estimated the degree of surface dirt.

With no white muddiness by A fingerprint adhesion (20% or less of haze value)

White muddiness arose by B fingerprint adhesion (not less than 30% of haze value).

[0068]** It was based on drop test JIS Z 0202. Water was filled in the container, the concrete floor surface was dropped from 120 cm in height, and, specifically, this was performed. After performing fall about ten water filling containers and ten vertical drops' carrying out to one container on condition of a room temperature, ten flat dropping carried out. The valuation basis is as follows.

A With no breakage container.

Not less than 80% of the complete vessels with which B breakage container presented the drop test

[0069]** From the pars basilaris ossis occipitalis of the container which comprises the measuring method cyclic olefin system copolymer of a relaxation state, the sample was started from a 20-mm position to 10 mm squares, minute X-ray diffractometer (PSPC-150C) (product made from Physical science Electrical and electric equipment) used, and the relaxation state was measured. The height direction of the container was made into the height direction of a measuring plane, and direction of a sample set it. The measuring condition was performed on the tube voltage of 30 kV, tube current of 100 mA, and the conditions for measuring time 200 seconds. Integrated-intensity calculation was performed in 7.241 to 23.241 degrees after measurement, and it asked for half peak width.

[0070]The injection-blow-molding machine (ISK881-F85, product made by Kerplas) was used, and melting blow molding of comparative example 1 cyclic-olefin system copolymer APL6508T (product made from Mitsui Petrochemistry) was carried out to 5K standard tablet bottle of 15.2 g of metsukes at the temperature of 140 °C. The haze value was 8.1% when the haze value was measured about the obtained container. Next, the haze value was 15.1% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the obtained container. It turned out that there is surface dirt by fingerprint adhesion by the evaluation A, and it excels in resistance to contamination. Next, the result of a drop test is the evaluation B and it turned out that it is inferior to shock resistance. Said examination ** was performed. These results are shown in Table 1.

[0071]A biaxial-stretching-blow-molding machine (Nissei ASB-50H, product made from Nissei

ASB Machine industry) is used for comparative example 2 cyclic-olefin system copolymer APL6508T (product made from Mitsui Petrochemistry), Extension shaping was carried out at 5K standard tablet bottle of 10.5 g of metsukes on conditions 4 to 5 times the draw magnification [the temperature of 100 **, and] (area magnification) of this. The fitness extension molding temperature of this cyclic olefin system copolymer is 95 thru/ or 105 **. At a temperature lower than 95 **, the white blush mark was produced at the pars basilaris ossis occipitalis, and, on the other hand, the shock-proof fall was produced by orientation relaxation at a temperature higher than 105 **.

The haze value was 3.9% when the haze value was measured about the obtained container. The haze value was 83.7% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the obtained container. The surface dirt by fingerprint adhesion is the evaluation B, and it turned out that it is inferior to resistance to contamination. Next, the result of a drop test is the evaluation A and it turned out that it excels in shock resistance. Said examination ** was performed. These results are shown in Table 1.

[0072]A biaxial-stretching-blow-molding machine (Nissei ASB-50H, product made from Nissei ASB Machine industry) is used for embodiment 1 cyclic-olefin system copolymer APL6508T (product made from Mitsui Petrochemistry), Extension shaping was carried out at 5K standard tablet bottle of 10.5 g of metsukes on conditions 4 to 5 times the draw magnification [the temperature of 100 **, and] (area magnification) of this. Using the reducing flame of a gas burner, 20 mm at intervals of the burner and the container drum part, the container was passed by the earliness of 6 cm/min and the drum section of this extension molded container was heat-treated. Skin temperature was 158 **, when the heat conductive pair was stuck to the specimen container on the Kapton tape at this time and the container surface temperature at the time of heat-treatment was measured. The haze value was 14.5% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the container after processing. The surface dirt by fingerprint adhesion is the evaluation A, and it turned out that it excels in resistance to contamination. Next, the result of a drop test is the evaluation A and it turned out that it excels in shock resistance. Said examination ** was performed. These results are shown in Table 1.

[0073]It carried out like Embodiment 1 except the interval of embodiment 2 burner and a container drum part having been 30 mm. The container surface temperature at the time of heat-treatment was 144 **. The haze value was 18.7% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the container after processing. The surface dirt by fingerprint adhesion is the evaluation A, and it turned out that it excels in resistance to contamination. Next, the result of a drop test is the evaluation A and it turned out that it excels in shock resistance. Said examination ** was performed. These results are shown in Table 1.

[0074]It carried out like Embodiment 1 except having made the transit rate of comparative example 3 container into 3 cm/min. The container surface temperature at the time of heat-treatment was 246 **. Although modification of a container was seen, the haze value was 18.4% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the container after processing. The surface dirt by fingerprint adhesion is the evaluation A, and it turned out that it excels in resistance to contamination. However, the result of a drop test is the evaluation B and it turned out that it is inferior to shock resistance. Said examination ** was performed. These results are shown in Table 1.

[0075]It carried out like Embodiment 1 except the interval of comparative example 4 burner and a container drum part having been 50 mm. The container surface temperature at the time of heat-treatment was 68 **. The haze value was 81.7% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the container after processing. The surface dirt by fingerprint adhesion is the evaluation B, and it turned out that it is inferior to resistance to contamination. However, the result of the drop test was the evaluation A. Said examination ** was performed. These results are shown in Table 1.

[0076]A biaxial-stretching-blow-molding machine (Nissei ASB-50H, product made from Nissei ASB Machine industry) is used for embodiment 3 cyclic-olefin system copolymer APL6508T (product made from Mitsui Petrochemistry), Extension shaping was carried out at 5K standard tablet bottle of 10.5 g of metsukes on conditions 4 to 5 times the draw magnification [the preforming temperature of 115 **, the skin temperature of 40 ** of the drum section corresponding point of a metallic mold, and] (area magnification) of this. The tablet bottle after shaping was held for 3.5 seconds in the metallic mold, and the internal and external molecular orientation grant and molecular orientation relaxation by temperature distribution were performed, blowing cold blast into the inside of a bottle. The haze value was 18% when spreading of petroleum mixture WD-40 and measurement of the haze value were performed about the obtained container. The surface dirt by fingerprint adhesion is the evaluation A, and it turned out that it excels in resistance to contamination. Next, the result of a drop test is the evaluation A and it turned out that it excels also in shock resistance.

[0077]

[Table 1]

ボトル	表面 温度	指紋 付着	ヘーズ値 (%)	落下 試験	半価幅	積分 強度	積分幅	ピーク 位置
比較例 1	—	A	15.1	B	5.603	286670	6.179	19.742
比較例 2	—	B	83.7	A	5.943	209372	6.204	15.945
実施例 1	15.8	A	14.5	A	5.693	211043	6.346	16.657
実施例 2	14.4	A	18.7	A	5.752	251458	6.291	16.937
比較例 3	24.6	A	18.4	B	5.644	250592	6.168	16.839
比較例 4	6.8	B	81.7	A	5.674	206027	5.489	16.882

[0078]

[Effect of the Invention] In this invention, orientation relaxation of the cyclic olefin system copolymer of the thin layer of an outside surface is carried out so that a haze value when a spreading examination is done with a specific petroleum mixture may be less than 20%. Therefore, generating of the dirt by fingerprint adhesion of an outside surface can be prevented thoroughly.

And since it was restricted to the surface thin layer that molecular orientation relaxation is carried out and molecular orientation remains in the cyclic olefin system copolymer of most container walls, the advantage of being maintained without shock resistance falling on parenchyma is also acquired.

[Translation done.]